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## Catalytic Soot Oxidation studied by ETEM

S.B. Simonsen<sup>1\*</sup>, S. Dahl<sup>1</sup>, E. Johnson<sup>2</sup>, A.M. Molenbroek<sup>1</sup>, I. Chorkendorff<sup>3</sup> and S. Helveg<sup>1</sup>

*1Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, (Denmark)*

*2Nano-Science Center, University of Copenhagen, DK-2100 Copenhagen (Denmark)*

*3 CINF, Technical University of Denmark, DK-2800 Kgs. Lyngby (Denmark)*

*\*sbrs @topsoe.dk*

### Introduction

Focus on challenges in diesel emission exhaust reduction (e.g. catalyst sintering and removal of soot) is increasing. Here environmental transmission electron microscopy (ETEM) is used for monitoring such processes with focus on soot oxidation.

An attractive approach for effective soot removal includes the introduction of filters on the diesel-driven vehicles and the fictionalization of the filters for catalytic soot oxidation [1,2]. Ceria-based materials are widely adopted for this purpose. It is generally accepted that the redox properties of ceria are crucial to the catalytic effect, but the detailed reaction mechanism and the location of the catalytic active sites are still being debated. For instance, it has been proposed that the reaction occurs at the soot-ceria interface [3] and that the reaction occurs through spill-over of oxygen from ceria to reaction centers located at the soot surfaces [2-4].

Averaging techniques, such as temperature-programmed oxidation and thermogravimetric analysis, have mainly been used to study the soot oxidation reaction, e.g. [2-5]. Although these studies provide significant insight, previous work on metal-catalyzed gasification of graphite suggests that ETEM may be a beneficial complement, because the technique allows direct observations at the carbon-catalyst interface to be obtained in situ during reaction [6]. In this contribution we present an ETEM study of the reaction mechanisms and kinetics involved in ceria-catalyzed soot oxidation related to diesel engine emission control [7].

### Materials and Methods

ETEM has become a powerful tool in heterogeneous catalysis due to its ability to directly monitor catalysts in situ during exposure to reactive gases at elevated temperatures. The present experiments were performed using a CM300 FEG ETEM [8], or a Titan 80-300 image aberration-corrected ETEM, from FEI Company. To model soot deposited in a diesel particulate filter, a carbon black (CB) powder of particles with a diameter of about 30nm (Printex U, Degussa GmbH) was mechanically mixed with a CeO<sub>2</sub> catalyst powder (or with an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reference powder) with a volume ratio 1:10.

In the ETEM, the CB-oxide samples were exposed to ca. 2 mbar O<sub>2</sub> and a temperature in the interval 300-600°C. The samples were monitored by acquisition of time-lapsed ETEM image series (movies) using a low-light and fast-scan CCD camera. The electron beam current density was kept below 0.16A/cm<sup>2</sup>, which was sufficiently low to avoid influence of the electron beam on the CB oxidation kinetics.

## Results and Discussion

The ETEM movies provide direct observations of soot particles in contact with catalytically active  $\text{CeO}_2$  (or inert  $\text{Al}_2\text{O}_3$ ) during exposure to an oxidizing gas environment. The results show that the catalytic oxidation reaction involves processes confined to the soot- $\text{CeO}_2$  interface region, and that the catalytic reaction surprisingly results in motion of soot agglomerates toward the catalyst surface (fig. 1), which acts to continuously re-establish the soot- $\text{CeO}_2$  interface in the course of the oxidation process.

The observed reaction dynamics is found to consistently explain observations from *ex situ* oxidation experiments. Moreover, a quantitative analysis of ETEM movies obtained at different reaction temperatures demonstrates that the apparent activation energy of  $\text{CeO}_2$ -catalyzed soot oxidation can be measured with ETEM for a more well-defined tight physical contact situation and is quantitatively in good agreement with previous kinetic studies, e.g. [3].

## Significance

The first ETEM observations of the ceria-catalyzed soot oxidation reveal that the reaction mechanism involves reaction centers located near the soot-ceria interface.

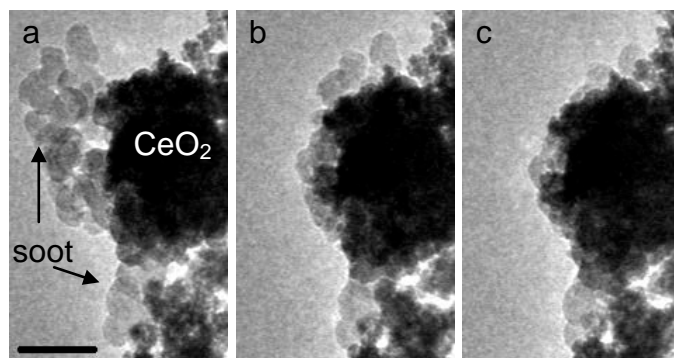


Figure 1: A time-lapsed ETEM image series of soot in contact with a  $\text{CeO}_2$  catalyst acquired during the exposure to 2 mbar  $\text{O}_2$  at  $550^\circ\text{C}$ . The time interval between the images is  $\sim 2\text{min}$ . Scale bar, 90nm. The figure is adapted from [7].

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